



Surface and mechanical properties of hydrophobic silica contained hybrid films of waterborne polyurethane and fluorinated polymethacrylate



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ABSTRACT

The surface and mechanical properties of hybrid films of waterborne polyurethane (WPU) and fluorinated polymethacrylate (FPMA), and high-hydrophobic silica (SiO₂) contained hybrid films of FPMA/WPU were investigated. X-ray photoelectron spectroscopy confirmed that the surfaces of hybrid films exhibited notable fluorine enrichment. Scanning electron microscopy observation demonstrated that micro-scale rough structures consisted of sub-micro papillae and micro-scale wrinkles formed on the surfaces of FPMA/WPU. This was attributed to the enhanced phase separation of WPU and the incompatibility of low-surface-energy FPMA and WPU. Colloidal SiO₂ was modified by polydimethylsiloxane and the modified SiO₂ was reactive and high-hydrophobic. After the addition of reactive SiO₂, the rough structures became micro-scale striped wrinkles studded with nano- and sub-micro papillae formed by the high-hydrophobic SiO₂. The combination of the fluorine enrichment and the rough structures accounted for the high hydrophobic FPMA/WPU film and superhydrophobic SiO₂/FPMA/WPU film.

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1. Introduction

Waterborne polyurethane (WPU) that is nontoxic, nonflammable, low-temperature resistance, flexibility, and friendly to the environment has been widely used for various applications, such as adhesives and coatings [1–4]. However, WPU has some drawbacks, such as relatively low heat-resistance, poor mechanical properties, as well as weak water-resistance, which inhibit its extensive application [5–8]. To compensate for these drawbacks, many researchers modified WPU by cross-linking reaction and hybridization with organic polymers and inorganic nanoparticles, such as epoxy, fluoroalkyl silane, siloxane and silica (SiO₂) [9–16].

Levine et al. [11] reported the WPU military topcoat with an emulsion of fluoroethylene vinyl ether polyol (FVP). As measured using X-ray photoelectron spectroscopy (XPS), fluorine enriched at the air interface was as high as 90 times the bulk concentration. As expected, water contact angle increased approximately in a linear fashion with the surface fluorine concentration and reached about

90° at the 15% fluorine atomic concentration. When the addition of FVP reached or exceeded 10% of the polyol fraction, mechanical properties and resistance to weathering were significantly reduced. Lee et al. [12] reported WPU/perfluorodecyl acrylate hybrid materials. Their mechanical properties and water contact angles increased with increasing perfluorodecyl acrylate content. When the mass ratio of WPU and perfluorodecyl acrylate was 7 to 3, the lowest surface energy (18.18 mN/m) and the highest contact angle (111.76°) of the hybrid film were achieved. Bai et al. [13] introduced polysiloxane groups with low surface energy into the soft segment of a UV crosslinkable WPU. Their water resistance, thermal property, and mechanical property were improved and the contact angle reached 97.8°. Kim et al. [14] reported that fluorinated polyurethane (PU) was blended with base PU prior to dispersion in water to modify the surface of UV cured WPU. Atomic force microscopy (AFM) showed that the surface was roughened with the addition of fluorinated PU. After the addition of 9 wt % fluorinated PU, the contact angle reached 92.6° and their hardness and mechanical properties were marginally altered. Jeong et al. [15] modified conventional PU dispersion by blending the base PU and fluorinated urethane oligomer prior to water dispersion. Surface roughness of the cast film increased over 13 times according to

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AFM tests, and the contact angles with water and methylene iodide were beyond 90° after the addition of 15% fluorinated urethane oligomer. Zhai et al. [16] reported the SiO₂/WPU hybrids prepared by in situ hydrolysis and condensation of tetraethyl orthosilicate (TEOS). Their water resistance and tensile strength were improved after the addition of TEOS. The advancing contact angles of the hybrids with 7.5 wt % TEOS reached 101.2°.

Although the hydrophobic properties of the modified WPU are greatly improved, there is still space for further improvement in the hydrophobic properties compared with the superhydrophobic materials with micro/nano structures [17–20]. It is well known that the high hydrophobicity of a surface can be enhanced in two ways: one is to create rough structures on the surface with low surface energy and the other is to modify the surface with rough structures using low surface energy materials, such as fluorinated polymers, siloxane and fluoroalkyl silane [19–26]. However, according to the above reports [11–16], the surface roughness of the modified WPU is still insufficient, that is, their surfaces do not form effectively rough structures, which hinders the improvement of hydrophobic properties.

In this work, surfaces with rough structures of fluorinated polymethacrylate (FPMA)/WPU and SiO₂/FPMA/WPU were prepared by taking advantage of the difference in solubility of WPU and FPMA in water, micro-phase separation and high hydrophobic SiO₂. Importantly, both water resistance and mechanical properties of hybrid films were improved significantly.

2. Experimental

2.1. Materials

Colloidal SiO₂ with a mean size of 20 nm was supplied by Jingye Nanotechnology Co., Ltd. (China). Dimethylol propionic acid (DMPA) was obtained from Aladdin Reagent (Shanghai, China). Polytetramethylene glycol (PTMG, Mn = 2000), and 4, 4-diphenyl methane diisocyanate (MDI) were supplied by An Li Artificial Leather Co., Ltd., Hefei, China. Benzoyl peroxide (BPO), acetone, triethylamine (TEA), butanediol (BD), and N, N-dimethylformamide (DMF), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Dodecafluoroheptyl methacrylate (FMA) was supplied by XEOGIA Fluorine–Silicon Chemical Co., Ltd. Polydimethylsiloxane (PDMS, Mn = 400, C_{OH} = 280 mg KOH/g) was obtained from Foshan Vago Organic Silicon Co., Ltd., Guangzhou, China.

2.2. Modification of SiO₂

PDMS and SiO₂ were heated at 100 °C under reduced pressure (5 Torr) for 6 h. Then, PDMS and SiO₂ with the mass ratio of 1 to 1 were put into an autoclave and mixed by stirring. After mixing, they were sealed in the autoclave under nitrogen atmosphere and heated at 200 °C for 8 h. The treated SiO₂ were repeatedly washed using acetone and benzene by vacuum filtration. The filtrate cake was placed in a vacuum oven at 90 °C for 12 h. At last, the dried cake was ground and sieved with a 325 mesh sieve to obtain the PDMS-modified SiO₂.

2.3. Preparation of FPMA/WPU and SiO₂/FPMA/WPU hybrid emulsions

The sample designation and theoretical composition are summarized in Table 1. As for the FPU-1 (Scheme 1), 10.0 g of MDI, 20.0 g of PTMG, 2.68 g of DMPA, 4.0 g of FMA and the radical initiator (BPO: 2 wt% based on the FMA weight) were put into a 500 ml three-necked flask equipped with a condenser tube, dropping funnel, and mechanical stirrer to react at 80 °C for about 3 h under nitrogen atmosphere. Then the mixture of NCO-terminated prepolymers and FPMA oligomers were obtained. The change in the

Table 1

Sample designation, composition, carbonyl hydrogen bonding index (*R*) and degree of phase separation (DPS) in samples.

Sample designation	Composition (g)							<i>R</i> (%)	DPS (%)
	MDI	PTMG	DMPA	BD	TEA	FMA	SiO ₂		
FPU-0	10	20	2.68	0.9	2.1	0	0	27	21
FPU-1	10	20	2.68	0.9	2.1	4	0	85	46
FPU-2	10	20	2.68	0.9	2.1	8	0	90	47
FPU-3	10	20	2.68	0.9	2.1	4	1.78	71	42
FPU-4	10	20	2.68	0.9	2.1	8	1.78	76	43

NCO value during the reaction was determined by the standard dibutylamine titration method (HG/T 2409-92). According to the NCO value determined by the method, a stoichiometric amount of BD dissolved in 40 ml acetone was added dropwise to extend the chain at 60 °C until the theoretical NCO content was reached. After that, the reaction mixture was cooled to 50 °C, and 2.1 g of TEA was added to neutralize the carboxylic groups of DMPA. After 30 min neutralization, distilled water was added to the mixture with vigorous stirring to obtain the FPMA/WPU hybrid emulsion with the solid content of about 28 wt %. Other FPMA/WPU (FPU-2) and SiO₂/FPMA/WPU (FPU-3, FPU-4) hybrid emulsions were prepared in the similar way.

2.4. Characterizations

IR spectra of the cast films on KBr pellet were recorded on a Nicolet Nexus Fourier transform infrared (FTIR) spectrometer. Thermal gravimetric analysis (TGA) was carried out using a Q5000 IR thermal gravimetric analyzer at a heating rate of 10 °C/min under air condition. Mechanical properties were measured using an instron universal material testing system (model 5567) at room temperature with gauge length of 30 mm and crosshead speed of 100 mm/min. Dynamic viscoelastic behaviors of samples were investigated using a dynamic mechanical analyzer (Pyris Diamond DMA) with a heating rate of 2 °C/min at a frequency of 5 Hz. Contact angles of the films with deionized water drop were measured with a contact angle goniometer (G-1, Erma) at room temperature. To measure swelling in water, films were immersed in water for 72 h at 25 °C. The water swelling of the films was calculated by using the following equation:

$$\text{Swelling}(\%) = 100(W - W_0)/W_0 \quad (1)$$

where W_0 is the weight of the dried film and W is the weight of the film at equilibrium swelling. The morphology of samples was observed under a Sirion-200 (FEI, America) scanning electron microscopy (SEM) with an accelerating voltage of 10 kV. The samples for SEM observation were prepared by casting the polymer emulsions onto a clean glass disk and the disk was put into an oven at 100 °C for 12 h. Surface compositions were analyzed on an angle-dependent XPS (Perkin–Elmer physical electronic model 5400) with a hemispherical analyzer and a position sensitive detector. The spectrometer was equipped with a Mg K α achromatic X-ray source (300 W, 14 kV) and take off angle of 30° was used with the X-ray source. The samples for XPS tests were prepared by casting the polymer emulsions onto a clean glass disk. The disk was put into an oven at 100 °C for 12 h.

3. Results and discussion

3.1. FTIR spectra and phase separation

FTIR spectra were used to characterize the PDMS-modified SiO₂ as shown in Fig. 1. The FTIR spectrum of PDMS showed a strong Si–

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